Recent Developments in the Stripping Voltammetric Determination of Indium

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Abstract The determination of indium has become increasingly more important as the demand for this metal has greatly increased in recent years for the manufacture of touch screen devices, photovoltaic and semi-conductor devices. Concentrations of In generally reported in the environmental are very low requiring highly sensitive techniques such as stripping voltammetry to obtain the detection limits required. This present review focuses on the past and present applications of stripping voltammetry for the determination of In. The majority of applications have utilized Hg working electrodes, either as hanging Hg drop or as thin-film electrodes for use in either anodic stripping voltammetry or adsorptive stripping voltammetry. Detection limits in the low ng/mL range have been generally been reported. The major issue with In determination has been its very low concentrations and interferences from elements such as Pb and Cd, which are generally found in much greater concentrations. More recently alternatives such as Sb and Bi thin film electrodes have been reported and shown to give similar or superior performance characteristics.

Keywords: indium, anodic stripping voltammetry, adsorptive stripping voltammetry, bismuth, mercury, antimony

1. Introduction

A number of reviews have been recently given regarding the electrochemical determination of metals such as Pb [1] and other heavy metals at a variety of different electrode materials, such as screen-printed [2,3] Bi $[1,4,5]$ and Hg $[6]$. However, this represents the first review focused on the stripping voltammetric determination of In. The demand for indium has increased dramatically due to the identification of new applications in the rapidly growing electronics, photovoltaic, and touch-screen technology markets [7]. This increased demand has led to increase interest in the determining In levels in a range of matrices, such as river water [8] and for occupational monitoring [9] with a number of studies reporting the pulmonary toxicity of InP and InAs [10,11] both widely used in the electronics industries. Recently, countries, such as Taiwan have set limits for In levels in drinking water of 70µg/L and the Japan Society for Occupational Health recommended a value of 3μg/L in serum as the occupational exposure limit [12]. Methods which are both sensitive and reliable are required for its determination. The oral toxicity of In has been shown to be low [13] and In has been cited as a potential health supplement $[14,15]$ and can be presently purchased from many different internet sources.

A number of different analytical techniques have been employed, including inductively coupled spectroscopy and atomic adsorption spectroscopy. However, these require well equipped laboratories and highly trained personal for their application. Several electrochemical methods have

been reported [16-37]. These offer a number of advantages, as these require only an appropriate power supply and can be used on-site by relatively untrained operators.

The present review has been divided by the working electrode material utilised. The majority of applications have utilised Hg based working electrodes, as either hanging Hg drop electrode (HMDE) or as thin Hg film electrodes (TMFEs). A number of more recent applications have utilised alternative metals such as Sb and Bi. Several applications have utilised In as an internal standard [23,24] for the determination of other metal ions.

2. Mercury Working Electrodes for the Determination of Indium

In exhibits a relatively high solubility in Hg (69.1 % at. for a saturated amalgam $[25]$ and the redox transfer of three electrons contribute to a high sensitivity which can be achieved with the use of mercury electrodes. Vydra *et al* [6] have reviewed the early applications of Hg based electrodes for the stripping voltammetric determination of In. In mineral acids containing anions such as Cl, Br, I and SCN the reduction potentials shift to more positive potentials. In forms an intermetallic species with Au and consequently Au substrates are generally avoided. Reportedly, at Hg In can be determined in a range of different electrolytes (NaCl, $(NH_4)_2SO_4$, KOH, HCl, HNO3, oxalic, citric, tartaric acids, NH4F, LiOH and HBr), which under the conditions investigated NH_4F and HNO_3 were reported to give the largest peak currents. However, halide containing electrolytes have been reported to give

enhanced sensitivity due to the increased reaction rate in this media and in solutions of HCl, KCl or $HNO₃$ In levels as low as 10^{-9} M can be determined [6]. However, utilising supporting electrolytes of 0.5 M NH4Br with a 30 minute accumulation time In levels of $5x10^{-10}$ M are reportedly detectable [6].

The anodic stripping voltammetric (ASV) determination of In is generally hampered by being closely bracketed by Cd and Pb, metals which are generally in higher concentrations than that of In. A number of different methods have been utilised to overcome this problem, such as by the addition of potassium iodine or ethylenediamine can used to separate the In peak from Cd $[6]$. Wikiel and Kublik $[26]$ have utilised changes in the thickness of the deposited Hg film and the scan rate to control the resolution between stripping peaks and were able to show the possibility of resolving In from Tl, Cd and Pb. The catalytic active of *N*methylthiourea towards the reduction of In has also been explored as a method to improve the resolution between Pb and Cd [27]. Utilising such an approach it was possible to determine $3x10^{-7}M$ In(III) in the presence of $5x10^{-5}M$ Cd(II) and $1x10^{-4}M$ Pb(II) in 5M NaClO₄ at pH 2 by square wave voltammetry. Calibration curves for In(III) were reported to be linear from 3.9×10^{-7} to 5×10^{-4} M, with the relative standard deviation for the determination of In(III) reported as being about 3.0%. Liquid/liquid extraction prior to voltammetric analysis has been shown by Labuda and Vanickova [28] as an alternative method. Traces of Cd, Pb, Tl and In were extracted from aqueous solution by benzene or chloroform after the addition of Na or Zn diethyldithiocarbamate. Stripping voltammetry of Cd, Tl and Pb at a HMDE or TMFE was then undertaken in benzene/methanol medium (1:1) with 0.1M NaClO, as supporting electrolyte for Cd, Pb and Tl. For In, the medium was chloroform/ethanol/water (1:4:1) with 5mM sodium acetate/60mM KBr/60mM HCl as supporting electrolyte. In calibration graphs are linear at concentrations of about $10^{-7}M$ with a detection limit of $1x10^{-8}$ M.

Investigations of environmental samples by Florence e*t al* [19] have reported a separation method based on the coprecipitation of In on ferric hydroxide, followed by anion exchange chromatography from chloride media to eliminate Cd and Pb. Interferences were reported from Mo, Pt, PO_4^3 and high concentrations of Cu. The determination of In at TFMEs was found to greatly affected by the presence of dissolved oxygen and Pt. The environmental water samples investigated in the study were found to have levels below the reported detection limit of $5x10^{-4}$ µg/L In.

Reportedly there is marked difference in the behaviour of In at the HMDE and TMFE towards In in HCl solutions, where In did not form a deposit at a TMFE from 1M HCl [29]. Also, if electrolysis was carried out in an acetatebromide solution, and this electrolyte replaced with 1M HCl for the stripping step, no indium peak was obtained. They concluded that a particular chemical species of In(III) must be present before it can be reversibly deposited at a thin mercury film electrode. Bromide and iodide electrolytes were found to give larger stripping currents at the TMFE than chloride electrolytes. At the HMDE, a smaller increase in sensitivity in bromide and iodide media was reported. These results were concluded to be

due to double layer effects which appear to be far more important at the TMFE than at the HMDE, and that specifically adsorbed bromide or iodide greatly accelerates the reduction of In(III) at TMFEs.

Wang *et al* [30] have used a thin film Hg modified screen-printed carbon electrode (TMF-SPCE) and mercury-coated carbon-fibre electrode for the determination In by potentiometric stripping and chronopotentiometry. In was utilised as microrod "tag" for the determination of DNA hybridization. The cylindrical microrod metal particles were prepared by a templatedirected electrochemical synthetic route involving plating of In into the pores of a host membrane. The resulting μ m long rods were shown to offer a lower detection limit (250zM), as compared to common bioassays based on spherical nanoparticle tags. In was selected as the metal marker because it offers attractive electrochemical stripping behaviour and is not normally present in biological samples or as an impurity in related reagents. The DNA-linked particle conjugate in 10µL of 6M nitric acid (for 45 minutes) and transferring this solution to a 100µL acetate buffer (0.2M, pH 5.9) solution. Derivative chronopotentiometric measurements of the dissolved indium tracer were performed at a mercury-coated carbonfibre electrode prepared by pre-plating mercury for 10 minutes at -1.1V from a quiescent 0.1M HCl solution containing 100mg/L Hg(II) ions. The In deposition proceeded for 2 minutes at -0.9V; subsequent stripping was carried out after a 5s rest period, using an anodic current of $+1.0 \mu A$. The raw chronopotentiometric potential-time curve was converted into a peak-shaped dt/dE vs. E signal, and the data were filtered (by an 8 point "moving average" filter). Well-defined and sharp indium peaks were reported (Ep)-0.59V; $b_{1/2} = 29 \text{mV}$).

3. Adsorptive Stripping Voltammetry

Farias *et al.* [17] determined In by adsorptive stripping voltammetry (AdSV) with morin at a static Hg drop electrode. To avoid the interference of Pb and Al, they analysed the samples after precipitating and masking these elements.

An accumulation time of 60s at an applied potential of - 0.30V (vs. Ag/AgCl) was found optimum, with a final potential, -1.00V. Measurements were undertaken using a linear sweep waveform utilising a scan rate of 200mV/s in an acetate buffer (0.1M, pH 3.5) supporting electrolyte with a morin concentration of $1x10^{-5}M$. The response of the system was found to be linear over the range 4ng/mL to 40ng/mL In. A detection limit of 0.4nM (0.05ng/mL)

was reported for a 5 minute accumulation time. The method was applied to a sample of jarosite (an industrial residue from the refinement of zinc ore), known to contain significant quantities of indium.

Benvidi and Ardakani [18] have utilised xylenol orange for the differential pulse cathodic AdSV determination of In at a HMDE. A supporting electrolyte of 0.05M acetate buffer solution, pH 3.9, containing 5.0mM xylenol orange with an accumulation potential of -0.20V (vs. Ag/AgCl) was found optimum. Using an accumulation time of 60s, the linear range was reported to be 0.1-10ng/mL with a limit of detection of 0.03ng/mL. Utilising a longer accumulation time of 5 minutes, the linear range was reported to be 0.04-10ng/mL with an associated limit of detection of 0.013ng/mL. Water samples were examined after filtration (Whatman no. 1 filter paper) and ultraviolet (UV) irradiation for 2h with a 160-W UV lamp. Alloy samples and jarosite were digested by heating in $HNO₃$ -HCl (1:3) with a few drops of concentrated hydrofluoric acid. Concentrated ammonia was added to precipitate the hydroxide of In, Fe, and Al. The solution was filtered, and precipitate was dissolved in 50ml of 2M HCl. The solution was diluted with water to 100ml in a 100-ml volumetric flask. Cathodic AdSV was undertaking using a differential pulse waveform using a starting potential of - 0.45V and an end potential of -0.75V.

Xylenol orange

Using this approach levels of 0.24ng/mL were found in Zayandeh Rood river water, and were found to be in good agreement with that found by atomic absorption spectroscopy after 100-fold pre-concentration step. Analysis of various alloy samples was reported to give a mean recovery of 100 %.

Paolicchi *et al*. [21] carried out the determination of In by differential pulse AdSV using ammonium pyrrolidine dithiocarbamate (APDC) as the complexing agent obtaining a detection limit of 1.3nM at a HMDE.

Ammonium pyrrolidine dithiocarbamate

The solution for the accumulation of In was formed by adding 200µL of a 0.1M APDC solution to a 19.8mL aliquot of acetic acid adjusted to pH 1. An accumulation potential of 0.52V was applied for 600s. The potential was then sweep from -0.6V to -0.8V. Nineteen different elements were investigated as potential interferences, and only Cd was found to interfere. The method was applied to tap, river, seawater and urine samples. A mean recovery of 105 % was obtained and good agreement was found with a certified water sample.

The 1-(2-pyridylazo)-2-naphthol complex of In has been accumulated on naphthalene in the pH range of 6.5- 11.5 [31]. After filtration, the solid mass is shaken with 8 mL of 1 M HCl and In was determined by differential pulse polarography (DDP). A detection limit is 0.2ppm (signal to noise ratio 2) and the linearity is maintained in the concentration range 0.8-125 ppm with a correlation coefficient of 0.9994 and relative standard deviation of 0.96%.

1-(2-pyridylazo)-2-naphthol

It was shown possible to determine In levels in samples of alloy and a number of diverse certified samples, including, vehicle exhaust particulates Pepperbush, Chlorella, human hair; and tea leaves after digestion in $HNO₃$ and filtration. Good agreement was found with expected values and a number of different potential interferences were investigated. Only EDTA and Fe(III) were found to interfere. The latter could be masked by adding 2mL of 5 % triethanolamine solution during the pre-concentration step.

Pyrogallol Red has recently been employed for the AdSV determination of In at a HMDE [16]. Under optimised conditions detections limits of 7nM and 4nM by staircase and square wave voltammetry respectively. linear ranges of 10^{-8} to $5x10^{-7}M$ by staircase voltammetry. A near six times increase in sensitivity was recorded by square wave voltammetry. The developed method showed good agreement with that obtained by ICP-AES for investigations levels of In present in Al alloys. Interferences from Al could be readily suppressed by the addition of NaF.

4. Bismuth Working Electrodes for the Determination of Indium

Hg electrodes have been widely used in many electrochemical applications, as has been demonstrated here. However, recent concerns regarding problems with toxicity and subsequent disposable [32] have led to alternative materials being sort. One popular alternative is Bi, which has recently been explored by Charalambous and Economou for the determination of In [33]. The stripping voltammetric behaviour of In was investigated at a bismuth-film electrode (BiFE) in the presence of both Cd and Pb by square wave anodic stripping voltammetry (SWASV). Glassy carbon electrodes were modified In situ with bismuth films by fortifying the sample with the required concentration of Bi(III) (normally $200 \mu g/L$) and simultaneously depositing Bi and the metals on the surface of the electrode at -1.2V. It was generally observed that both the resolution and the stripping peak heights were affected by the nature and the concentration of the supporting electrolyte. Acetate buffer provided the worst resolution between the cadmium and indium peaks. Adding 0.1M KCl and KSCN to the 0.1M acetate buffer slightly improved the resolution between the cadmium and indium peaks while 0.1M acetate buffer with 0.1M KBr provided the best resolution. The improvement in resolution was caused by a shift of the Cd peak potential upon change of the electrolyte system as the Pb and In peak potentials remained almost constant in all the electrolytes tested. As has been previously shown in the case of Hg electrodes, as the Bi film thickness increased, all the peaks became wider and both Cd and Pb peak decreased in height. In contrast, the In peak height increased as the Bi(III) concentration increased up to 400 µg/L. Both the peak heights and widths of Pb and Cd peaks were found to increase with square wave pulse height. Interestingly, the In stripping peak height was found to be independent of this. This was concluded to result from a difference in the formation of the binary alloy of In and the alloys of Cd and Pb with Bi but this phenomenon was not investigated further. Tap water and fertiliser samples (after acid digestion) were investigated, but were found to contain In concentrations below the detection limit of the method.

5. Antimony Working Electrodes for the Determination of Indium

Bobrowski *et al* [34] have recently reported on the application of a glassy carbon electrode modified with Sb thin film. The antimony film electrode (SbFE) was prepared in situ at a glassy carbon support from a complexing supporting electrolyte, a saturated solution of hydrogen potassium tartrate. In this medium, Sb(III) ions reportedly forms complexes with tartrate, preventing the precipitation of Sb as SbOCl that can reportedly occur in other supporting electrolytes. SWASV was utilised for the determination of Cd, Pb, Zn, Tl, In and Cu detection limits of 0.5-3.8µg/L. Using a deposition potential of -1.5V for 120s, a linear response from 10 to 100 μ g/L In(III) with an associated detection limit of 1.4µg/L was reported. However, it was found impossible to determine all the ions under investigated as there was insufficient resolution, especial between Tl, Cd, In and Pb.

A SbFE have been recently reported for the determination of In(III) and TI(I) ions in non-deaerated aqueous solutions by SWASV [35]. The SbFE was reported to give well-defined and resolved stripping peaks after a short deposition time. Detection limits were reported to be 2 and $8\mu g/L$, for TI(I) and In(III) respectively. A relative standard deviation of 3.8 % and 2.8 % for 70 μ g/L TI(I) and In(III) ions was reported (n = 10). A linear response was found over the concentration range 20 to $100 \mu g/L$ for both analytes. The method was shown to be successfully applied to the analysis of In and TI ions in river water and tap water.

Sopha *et al* [36] have explored the relative merits of Hg, Bi and Sb thin film electrodes for the chronopotentiometric stripping determination of In, Tl and Zn. The antimony film was deposited in situ on a carbon paste substrate electrode and employed in chronopotentiometric stripping mode in deoxygenated solutions of 0.01M hydrochloric acid (pH 2). The performance of the developed method was compared with constant current chronopotentiometric stripping and anodic stripping voltammetry. When compared with the Bi and Hg based methods, the thin film Sb carbon paste electrode (SbF-CPE) was reported to show better electroanalytical performance for the measurement of Zn and Tl. The determination of In at the SbF-CPE showed a linear response over the range 10 to $100 \mu g/L$ for a 120s deposition time. A reproducibility of 1.62 % for indium (III) $40 \mu g/L$, $n = 11$.

6. Carbon Working Electrodes for the Determination of Indium

Approaches utilising working electrodes without some form of a metal film for the determination of In have not been widely reported. Xiang *et al* [37] have demonstrated the possibility of determining In by AdSV at nafion modified glassy carbon electrode. A linear range of range of $1.0x10^{-9}$ to $1.0x10^{-7}$ M was reported, with an associated detection limit of $7.5x10^{-10}$ M. The glass carbon electrode was modified by first polishing successively with 1, 0.3, and 0.05µm alumina powder suspensions on a smooth cloth, followed by ultrasonication in a double-distilled water bath and ethanol bath alternately, then rinsed with water, and then allowed to air dry. The surface was modified by coating the disk with $10 \mu L$ of a 0.5% nafion solution. The film was then dried and rinsed with doubledistilled water prior to each determination. In was accumulated from 10mL aliquots of 0.01M acetate buffer solution (pH 5.0) under forced convection. An accumulation potential of -0.7V for 120s was reported to be optimum. Linear sweep voltammetry was undertaken from -0.7V to -0.2V at a scan rate of 100mV/s after the electrode was rinsed at -0.2V for 3 minutes to prepare it for next determination. The influence of ten common metal ions on a $1x10^{-8}M$ In(III) was investigated and only Fe(II) was found to adversely affect the assay.

Nafion

7. Conclusions

The determination of In is increasingly important as demand from applications such as touch screen technologies, photovoltaic cells and semi-conductors increases. Concentrations in the environment are generally extremely low requiring techniques that are highly sensitive. Stripping voltammetry has been shown to be one of the few techniques that are capable of determining these levels. Competing technologies such as ICP [38,39] and graphite furnace spectroscopy [40,41] have been reported to give superior detection limits, generally low sub ppb (ng/mL), but generally utilise a separate preconcentration step, and are relatively more expensive, necessitating well equipped laboratories for their use. As can be seen from the summary given in Table 1 the majority of stripping voltammetric methods reported have utilised Hg based working electrodes. However, more recently an increasing number of methods have utilised Bi or Sb based working electrodes, offering improves in health and safety and in some cases improvements in analytical performance.

Table 1. Summary of electrochemical stripping techniques used for the determination of In

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Technique	Working Electrode	Linear Range	Limit of Detection	Comments	Ref
AdSV	Static Hg drop	$4-40$ ng/mL	0.05 ng/mL	Adsorption of In-morin complex.	$[17]$
AdSV	HMDE	$0.04 - 10$ ng/mL	0.013 ng/mL	Adsorption of In-xylenol orange complex.	$[18]$
ASV	TMFE		$5x10^{-4}$ ng/mL	Co-precipitation of In on ferric hydroxide, followed by anion exchange chromatography from chloride media to eliminate Cd and Pb.	$[19]$
ASV	HMDE			Investigation on the effect of various surfactants on the stripping voltammetric behaviour of In, Sn, Pb, Cd and Tl.	[20]
AdSV	HMDE		1.3 nM	Adsorption of In-ammonium pyrrolidine dithiocarbamate.	[21]
ASV	Metal thin-film electrodes	0.5 to 2.5 µg/mL		Both Hg and Bi thin film electrodes investigated	$[22]$
ASV	HMDE	$3.9x10^{-7}$ to $5x10^{-4}$ M	$1x10^{-7}$ M	The catalytic active of N-methylthiourea towards the reduction of In	$[27]$
AdSV	HMDE or TMFE	10^{-7} M	$1x10^{-8}$ M	In extracted from aqueous solution by benzene or chloroform as diethyldithiocarbamate complex.	$[28]$
AdSV	HMDE	0.8 to 125 μ g/mL	$0.2 \mu g/mL$	Adsorption of 1-(2-pyridylazo)-2-naphthol complex.	[31]
ASV	BiFE	10 to 90 ng/mL and 2 to 16 ng/mL		Two linear ranges: $10-90$ ng/mL In(III) in the presence of 40 ng/mL Cd(II) and 80 ng/mL Pb(II). 2-16 ng/mL In(III) in the presence of 5 ng/mL Cd(II) and 10 ng/mL $Pb(II)$.	$[33]$
ASV	SbFE	10 to 100 ng/mL	1.4 ng/mL	Cd, Pb, Zn, Tl, and Cu also determined. Tartaric acid used as electrolyte overcome precipitation of Sb as SbOCl.	$[34]$
ASV	SbFE	20 to 100 ng/mL	8 ng/mL	TI(I) also determined.	$[35]$
ASV and constant current chronopotentiometric stripping	SbFE	10 to 100 ng/mL	2.4 ng/mL	$TI(I)$, $Zn(II)$ also determined.	$[36]$
AdSV	Nafion modified GCE	$1.0x10^{-9}$ to $1.0x10^{-7}$ M	$7.5x10^{-10}$ M		$[37]$
ASV	carboxylic multi-walled carbon nanotube modified electrode	5×10^{-8} to 5.0×10^{-9} M		Al(III) also determined. Recoveries >95 % reported for river water samples	$[42]$
ASV	HMDE		$0.1 \ \mu g/mL$	Various rat organs analysed after a single pulmonary exposure to In. Sn also determined	$[43]$

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